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ABSTRACT

The operator-equivalent method was employed to calculate the theoretical splitting of electronic energy levels $^{3}P_{2}$, $^{1}D_{2}$, $^{3}P_{2}$, $^{3}F_{3}$, $^{3}F_{4}$, $^{1}G_{4}$, and $^{3}H_{6}$ in Tm(C$_{2}$H$_{5}$SO$_{4}$)$_{3}$·9H$_{2}$O. Intermediate field corrections were made to $\alpha$, $\beta$, and $\gamma$. A first-order perturbation treatment on Tm$^{3+}$ ($\text{hf}^{12}$) in C$_{3h}$ symmetry, using crystal-field parameters $A_{2}^{0} < r^2 > = 13$ cm$^{-1}$, $A_{4}^{0} < r^4 > = -80$ cm$^{-1}$, $A_{6}^{0} < r^6 > = -32$ cm$^{-1}$, and $A_{8}^{0} < r^8 > = 300$ cm$^{-1}$, predicts the position of the crystal quantum states in reasonable agreement with experiment.
CRYSTAL FIELD SPLITTING OF ENERGY LEVELS
OF THULIUM ETHYL-SULFATE*

John B. Gruber and John G. Conway

University of California
Lawrence Radiation Laboratory
Berkeley, California

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INTRODUCTION

In a Tm(C₂H₅SO₄)₃·9 H₂O single crystal, where the Tm⁺³ configuration is 4f¹², the perturbing influence of the water and ethylsulfate groups on the energy-level system of the free ion can be calculated by expanding the crystal-field electric potential in a series of spherical harmonics. A first-order perturbation treatment is possible since the crystal field splitting of the various electronic levels is of the order of 100 cm⁻¹, whereas the spin orbit splitting between adjacent levels is generally greater than 1000 cm⁻¹. The work of Ketelaar has shown that the point symmetry at the metal-ion site in rare earth ethylsulfates is predominately C₃h. Johnsen² and the present authors³ have found C₃h point symmetry to be consistent with the interpretation of the Tm(C₂H₅SO₄)₃·9 H₂O absorption spectra. However, a few transitions were observed that are forbidden in C₃h symmetry but are allowed in C₃v symmetry. The theoretical splitting of 3H₆, 3F⁴, 3F⁵, 3F₂, 1G₄, 1D₄, and 3P₂ levels presented here is based on the experimental work of these investigators.

CALCULATION OF INTERMEDIATE-FIELD OPERATOR EQUIVALENTS

The potential energy of a ⁴f electron in the electrostatic field of the lattice is taken to be

\[ h_2^0 (3 Z^2 - r^2) + h_4^0 (35 Z^4 - 30 Z^2 r^2 + 3 r^4) + A^0 \]

\[ (231 Z^6 - 315 Z^4 r^2 + 105 Z^2 r^4 - 5 r^6) + A^6 (x^6 - 15 x^4 y^2 + 15 x^2 y^4 - y^6). \]

The contribution to the free-Tm⁺³ Hamiltonian consists of two expressions of this form, corresponding to the two ⁴f electron "holes". The

*This work was performed under the auspices of the U. S. Atomic Energy Commission.
quantities $A^m_n$ are characteristic of the lattice and appear with
the corresponding quantities $< r^n >$, the mean value of $r^n$ for a single $4f$
electron.

As Stevens has shown, within a given manifold of $J$ the matrix
elements of the potential form $V^m_n$ associated with the parameter $A^m_n$ are related
to the matrix elements of certain angular-momentum operators through a factor
$\theta_n < r^n >$. Here $\theta_n$ is the so-called "operator equivalent" factor, usually
written as $\alpha$, $\beta$, and $\gamma$ for $n = 2$, 4, and 6. This theory has been generalized
by Elliott et al. for all rare earth ions. Judd has given the equations for
evaluating the pure L-S operator equivalent for $Pr^{+3} (4f^2)$. He has tabulated
these values for $^3H_4$, $^1G_4$, $^3F_4$, $^3F_3$, $^1D_2$, $^3P_2$, and $^3P_1$ in the same paper with
the crystal-field-splitting results for $Pr^{+3}$ in $LaCl_3$. For $Tm^{+3} (4f^{12})$, the
L-S $\alpha$, $\beta$, and $\gamma$ may be calculated from the $Pr^{+3}$ set of equations. The only
difference will be a change in sign. However, L-S coupling breaks down in
$Tm^{+3}$, and it is necessary to consider intermediate coupling effects on the L-S
operator equivalents.

In an earlier paper the electronic energy levels for $Tm^{+3}$ in the
intermediate field were obtained from a plot of $E/F_2$ vs $\chi$, where $\chi = \zeta/F_2$,$\zeta$ is the spin orbit parameter used by Spedding, and $F_2$ is a Slater integral.
The best fit of theory to experiment was obtained at $\chi = 3$. The eigenvectors
at $\chi = 3$ for $^3H_4$, $^3F_4$, $^1G_4$, and $^3F_2$, $^3P_2$, $^1D_2$, used in calculating $\alpha$, $\beta$, and
$\gamma$ in the intermediate field were obtained from an IBM-650 program. The
eigenvectors for $^3H_6$ and $^1I_6$ were calculated by hand using Spedding's equations.
Table I includes values of operator equivalents for $Tm(C_2H_5SO_4)_3 \cdot 9 H_2O$ with
intermediate-field corrections in brackets.

Suppose we wish to calculate $\alpha$, $\beta$, and $\gamma$ for $^1G_4$ in an intermediate
field at $\chi = 3$. In a $4f^{12}$ configuration there are three $J = 4$ levels. We write

$$
\| ^1G_4 \rangle = 0.6119 \| ^3H_4 \rangle + 0.7260 \| ^1G_4 \rangle - 0.3137 \| ^3F_4 \rangle ,
$$

(1)

where 0.6119, 0.7260, and -0.3137 are the corresponding eigenvectors, and
$\| ^1G_4 \rangle$ corresponds to the intermediate field $^1G_4$. Now we have
\[
\begin{align*}
\langle 1g'_{4\gamma} | \alpha | 1g'_{4\gamma} \rangle &= (0.6119)^2 \langle 3h_{4\gamma} | \alpha | 3h_{4\gamma} \rangle + (0.7260)^2 \langle 1g_{4\gamma} | \alpha | 1g_{4\gamma} \rangle \\
+ (0.3137)^2 \langle 3f_{4\gamma} | \alpha | 3f_{4\gamma} \rangle - 2(0.3137)(0.6119) \langle 3h_{4\gamma} | \alpha | 3f_{4\gamma} \rangle - (2)
\end{align*}
\]

There will be no cross terms involving \( 1g_{4\gamma} \) with \( 3f_{4\gamma} \) and \( 3h_{4\gamma} \), since matrix elements between different spin states are zero. Each of the pure L-S operator equivalents in Eq. (2) can be evaluated from the equations given by Judd. It is possible to factor out \( 1g_{4\gamma} \), L-S \( \alpha, \beta, \) and \( \gamma \) expressions from the right-hand side of Eq. (2), which leaves a sum of numbers that denotes the importance of intermediate-field corrections to the L-S operator-equivalent values. In this way, \( 3f_{4\gamma}, 3f_{2\gamma}, 3p_{2\gamma}, 1d_{2\gamma}, \) and \( 3h_{6\gamma} \) operator equivalents were calculated. The \( 3p_{1\gamma}, 3f_{3\gamma}, \) and \( 3h_{5\gamma} \) operator equivalents are not affected by spin-orbit interaction.

**SELECTION OF PARAMETERS**

Having found \( \alpha, \beta, \) and \( \gamma \) for a particular level, we can now express the crystal splitting in terms of parameters \( A_n^m < r^n > \). These parameters were defined earlier. The values that these parameters can assume must be consistent with the point symmetry at the rare-earth ion in the lattice.

In addition to containing some physical significance as a scale factor for the crystalline electric potential, \( A_n^m \) is also the repository for errors due to neglect of configuration interaction and interactions between crystal quantum states of one \( J \) level with those of a nearby \( J \) level. Since configuration interaction has greater effect on \( J \) levels in the ultraviolet than in the infrared, the \( A_n^m < r^n > \) parameters can not be expected to be really constant in going from \( 3h_{6\gamma} \) to \( 3p_{2\gamma} \) some 38,000 cm\(^{-1}\) away. Likewise, somewhat different parameter values are needed if a simultaneous perturbation treatment is carried out on the \( 3f_{2\gamma}, 3f_{3\gamma}, \) and \( 3f_{4\gamma} \) levels and if a general second-order perturbation treatment is carried out.

If we neglect the effects mentioned in the preceding paragraph, the structure of \( 3p_{1\gamma} \) (split into 2 sublevels \( \mu = 0, \pm 1 \)) gives at once a preliminary value for \( A_2^0 < r^2 > \). Unfortunately, our photographic plates unambiguously confirmed only the position of the \( \mu = \pm 1 \) sublevel in \( 3p_{1\gamma} \). Another line appearing in both \( \sigma \) and \( \pi \) polarization with a line width of
some 10 cm\(^{-1}\) may have been 2 lines close together. More careful polarization experiments, in which the \(\sigma\) and \(\pi\) spectra are taken as a function of the rotation of the crystal, are necessary to confirm the actual energy value of the splitting. Parameters \(A_6^6 < r^6 >\) and \(A_6^0 < r^6 >\) were chosen so as to give the proper splitting of the \(\mu = 3\) and \(\mu = \pm 2\) sublevels in \(^3P_k\), \(^1G_k\), and \(^3H_6\). Parameter \(A_4^0 < r^4 >\) was chosen so as to give reasonable splitting of the \(^3P_2\), \(^3F_2\), and \(^3H_6\) levels. The best over-all fit for this first-order perturbation treatment was obtained by using \(A_2^0 < r^2 > = 13\ \text{cm}^{-1}\), \(A_4^0 < r^4 > = -60\ \text{cm}^{-1}\), \(A_6^0 < r^6 > = -32\ \text{cm}^{-1}\), and \(A_6^6 < r^6 > = 300\ \text{cm}^{-1}\).

FITTING TO EXPERIMENTAL DATA

A. The \(^3H_6\) Level (see Fig. 1)

The theoretical predictions for \(\mu = 0, \pm 1, 3\) are in good agreement with those crystal quantum states reported by experiment. The prediction of additional states between \(\pm 1\) and 3 has led us to restudy our plates. Our reported analysis included only those intense lines in which polarization was complete.\(^3\) As many as 3 or 4 weak lines appear between those due to transitions from the \(\pm 1\) and 3, but these are not well polarized. These lines may be due to sublevels \(\mu = 0', \pm 1', \) and \(\pm 2'\) in \(^3H_6\) as the theory predicts or satellite levels, but our experiments cannot really confirm this. Forbidden transitions observed in \(^3P_2\), \(^1D_2\), and \(^1G_4\) may also confirm these predicted states in the \(^3H_6\) level.

B. The \(^3F_4\) Level (see Fig. 2)

The splittings of the \(\mu = \pm 2\) and 3 are in reasonable agreement with experiment. However, the presence of the \(^3F_3\) some 200 cm\(^{-1}\) away will cause certain states to be depressed more than others. This may explain the relative position of the theoretical value of \(\mu = \pm 1\).

C. The \(^3F_3\) and \(^3F_2\) Levels (see Figs. 3 and 4)

Since \(^3F_3\) and \(^3F_2\) are separated by 400 cm\(^{-1}\), a simultaneous perturbation treatment is necessary in order to get better fit. Such a treatment may reverse the positions \(\mu = \pm 1, \mu = \pm 2\) in \(^3F_2\), now given as a result of first-order methods. As yet, \(\mu = 0\) has not been reported for either of these levels.
D. The $^1G_4$ Level (see Fig. 2)

The splitting between the lower $\mu = 3$ and $\mu = \pm 1$, between $\mu = \pm 2$ and $\mu = \pm 1$, and between $\mu = \pm 1$ and lower $\mu = \pm 2$ fits that found by experiment. The experimental positions of both $\mu = 3$ sublevels are reasonably well established. The theoretical value of upper $\mu = 3$ cannot be brought into better agreement by this present treatment. A slightly different set of parameters, $A_2^0 < r^2 > = 13 \text{ cm}^{-1}$, $A_4^0 < r^4 > = -90 \text{ cm}^{-1}$, $A_6^0 < r^6 > = -20 \text{ cm}^{-1}$, and $A_6^6 < r^6 > = 200 \text{ cm}^{-1}$ gives the following somewhat better agreement: $\mu = 2 = -79 \text{ cm}^{-1}$, $\mu = 1 = -50 \text{ cm}^{-1}$, $\mu = 2' = 23 \text{ cm}^{-1}$, $\mu 3 = 101 \text{ cm}^{-1}$, $\mu 3' = 166 \text{ cm}^{-1}$.

That a slightly different set of parameters fits theory better to data may be due to increased importance of configuration interaction on excited levels. However, the internal inconsistency within the $^1G_4$ may be due to interactions between crystal quantum states of $^1G_4$ with those in $^3F_2$, $^3F_3$, and $^1D_2$.

The $^1D_2$ Level (see Fig. 4)

The poor agreement can be partially remedied by considering interaction of $^1D_2$ with $^1I_6$. Our plates reveal lines between $^3P_1$ and $^3P_0$ and to the red of $^3P_0$ as possibly due to the $^1I_6$. The energy of $^1I_6$ above $^1D_2$ was taken to be 6000 cm$^{-1}$. Even when the total matrix of the crystal field interaction between $^1D_2$ and $^1I_6$ is considered, it is impossible to obtain good agreement with $^1I_6$ this far removed from $^1D_2$.

Judd has also obtained a poor fit for $^1D_2$ in the analysis of PrCl$_3$(Pr$^{3+}$,4f$^2$).$^6$ Although configuration interaction is known to be important for $^1D_2$, it is difficult to see in detail why this poor agreement occurs again in Tm$^{3+}$.

The $^3P_2$ Level (see Fig. 4)

Actually good agreement exists between theory and experiment. The experimental error in measuring the broad lines in the ultraviolet is some 13 cm$^{-1}$ in magnitude.
## Table I

Operator Equivalents in the Intermediate Field, \( \text{Tm}^{3+} (4f^{12}) \)

<table>
<thead>
<tr>
<th>Level</th>
<th>( \langle J \parallel \alpha \parallel J \rangle )</th>
<th>( \langle J \parallel \beta \parallel J \rangle )</th>
<th>( \langle J \parallel \gamma \parallel J \rangle )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^3P_1 )</td>
<td>( \frac{1}{5} )</td>
<td>[1.000]</td>
<td>0</td>
</tr>
<tr>
<td>( ^3P_2 )</td>
<td>( \frac{-1}{15} )</td>
<td>[1.095]</td>
<td>( \frac{-4}{7.27} )</td>
</tr>
<tr>
<td>( ^1P_2 )</td>
<td>( \frac{-22}{15 \cdot 21} )</td>
<td>[0.678]</td>
<td>( \frac{-4}{7.27} )</td>
</tr>
<tr>
<td>( ^3F_2 )</td>
<td>( \frac{-8}{21 \cdot 15} )</td>
<td>[1.636]</td>
<td>( \frac{2}{7.81} )</td>
</tr>
<tr>
<td>( ^3F_3 )</td>
<td>( \frac{-1}{90} )</td>
<td>[1.000]</td>
<td>( \frac{1}{45 \cdot 99} )</td>
</tr>
<tr>
<td>( ^3F_4 )</td>
<td>( \frac{-1}{126} )</td>
<td>[-1.357]</td>
<td>( \frac{1}{45 \cdot 77} )</td>
</tr>
<tr>
<td>( ^1G_4 )</td>
<td>( \frac{2}{11 \cdot 35} )</td>
<td>[1.799]</td>
<td>( \frac{46}{11 \cdot 45 \cdot 77} )</td>
</tr>
<tr>
<td>( ^1I_6 )</td>
<td>( \frac{2}{99} )</td>
<td>[0.995]</td>
<td>( \frac{-4}{11 \cdot 15 \cdot 99} )</td>
</tr>
<tr>
<td>( ^3H_6 )</td>
<td>( \frac{1}{99} )</td>
<td>[1.010]</td>
<td>( \frac{8}{3 \cdot 11 \cdot 14 \cdot 85} )</td>
</tr>
</tbody>
</table>

\(^a\) The pure L-S operator equivalent, \( \beta \), is zero for \( ^3P_2 \), since the corresponding Racah coefficient is zero. However, if we allow for intermediate coupling effects, the entry becomes \( (-4/7.27) [0.629] \).
ACKNOWLEDGMENT

We wish to express our appreciation to Dr. B. R. Judd for his valuable discussion and suggestions during the writing of this paper. We also extend thanks to Mr. J. D. Axe who checked several of the calculations.

REFERENCES


\[ \begin{array}{ccc|ccc|ccc}
\hline
\mu & \text{calc (cm}^{-1}\text{)} & \mu & \text{obs (cm}^{-1}\text{)} & \mu & \text{calc (cm}^{-1}\text{)} & \mu & \text{obs (cm}^{-1}\text{)} \\
\pm 2 & 102 & \pm 2 & 12763 & 3 & 199 & \\
3 & 49 & \pm 1 & 12720 & 3 & 101 & 3 & 21379 \\
\pm 1 & -18 & \pm 2 & 12649 & 3 & 12 & 21279 \\
\pm 2 & -62 & 3 & 12586 & 0 & 21255 \\
0 & -99 & & & & 21191 & 21168 \\
\hline
\end{array} \]
\[^3F_3\]

<table>
<thead>
<tr>
<th></th>
<th>calc (cm(^{-1}))</th>
<th></th>
<th>obs (cm(^{-1}))</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>±2 25</td>
<td>3</td>
<td>±2 14 486</td>
</tr>
<tr>
<td>3</td>
<td>±2 21</td>
<td>±1</td>
<td>±1 14 666</td>
</tr>
<tr>
<td>±1</td>
<td>-22</td>
<td>3</td>
<td>-35</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>3</td>
<td>14 407</td>
</tr>
</tbody>
</table>

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\[ \begin{array}{cccccc}
\text{\(\mu\)} & \text{calc} & \text{\(\mu\)} & \text{obs} & \text{\(\mu\)} & \text{calc} \\
(\text{cm}^{-1}) & (\text{cm}^{-1}) & (\text{cm}^{-1}) & (\text{cm}^{-1}) & (\text{cm}^{-1}) & (\text{cm}^{-1}) \\
0 & 82 & & & \pm 1 & 27971 \\
\pm 2 & 7 & \pm 2 & -38140 & \pm 2 & 27900 \\
\pm 1 & -48 & \pm 1 & -38060 & \pm 2 & 27876 \\
\end{array} \]

\[ \begin{array}{cccc}
\text{obs} & \text{\(\mu\)} & \text{calc} & \text{obs} \\
(\text{cm}^{-1}) & (\text{cm}^{-1}) & (\text{cm}^{-1}) & (\text{cm}^{-1}) \\
0 & 41 & \pm 1 & 15106 \\
\pm 2 & -24 & \pm 2 & 15079 \\
\end{array} \]

\[ \begin{array}{c}
\text{MU-19222} \\
\end{array} \]